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A DISSERTATION

SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY IN THE
UNIVERSITY OF MICHIGAN

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By J. P. COOLEY

ABSTRACT

Previous investigations on methane have shown three absorption regions which Coblentz places at $7.7\ \mu$, $3.31\ \mu$, and $2.35\ \mu$. By using the higher resolving-power of a grating spectrometer all of these have been partially resolved into lines. About fifty lines in the region of $3.31\ \mu$ were measured and arranged in positive and negative series. Between these, and masking part of the negative or longer wave-length series, lies a narrow region of intense absorption corresponding to the zero branch. Here the lines are too closely packed to be resolved but the complex structure is indicated by a large shift of the maximum absorption when the thickness of the layer of gas is changed. The band at $7.7\ \mu$ is similar to the one at $3.31\ \mu$. Twelve lines in the negative series and eighteen in the positive series have been measured but again in the zero branch no fine structure appears. The resolving-power of the apparatus was insufficient to show much detail in the band at $2.35\ \mu$. In the positive and negative branches near $7.7\ \mu$ the frequency difference between adjacent lines is $9.77\ \text{cm}^{-1}$ and near $3.31\ \mu$ it is $5.41\ \text{cm}^{-1}$. A faint band of twelve lines near $3.5\ \mu$ has a frequency difference approximating $15.3\ \text{cm}^{-1}$.

INTRODUCTION

John Tyndall,¹ in a characteristically interesting memoir published in 1862, presented the results of his researches on the absorption of undispersed radiation by gases. He showed that air, oxygen, nitrogen, and hydrogen are nearly transparent, whereas carbon monoxide, hydrogen chloride, methane, and other gases with more complicated molecules are fairly opaque. Many years later during a survey of the infra-red region with a prism spectrometer Angstrom² found absorption bands for methane near $2.12\ \mu$, $3.18\ \mu$, and $10.59\ \mu$.

¹ *Philosophical Transactions*, **152**, 59, 1862.

² *Öfversigt af Kongl. Vetenskaps-Akad. Förh.*, **47**, 331, 1890.

He concluded that the wave-length of maximum absorption shifts with the thickness of the absorbing layer of gas and that apparently Lambert's law does not hold. Coblentz,¹ however, pointed out that the wave-lengths greater than $5\ \mu$ published by Angstrom are very inaccurate, and he located simple absorption maxima for methane at $2.35\ \mu$, $3.31\ \mu$, and $7.7\ \mu$.

Rubens and von Wartenberg² have explored certain absorption spectra in the far infra-red by the method of *Reststrahlen*. They give the following results for a column of methane 40 cm in length:

Wave-Length	Transmission Percentage
23 μ	91.0
52	94.3
110	99.2
314	100.0

Recent advances in infra-red spectroscopy have made possible a detailed study of the bands located by these observers. In but few gases, notably *HF*, *HCl*, *HBr*, *H₂O*, *CO₂*, and *CO*, is the fine structure of the bands in this region known, and with some of these substances the complete data is still lacking. That such measurements are important is indicated by the great amount of theory that has been built on this rather meager foundation. Methane (*CH₄*) played an important rôle in the early history of stereochemistry, and the behavior of this gas led chemists to believe that, in the molecule, the four hydrogen nuclei occupy the corners of a regular tetrahedron with the carbon atom at the center. From the symmetry of such a model, simple band structure is to be anticipated; from a small moment of inertia about an axis through the center of gravity, widely spaced lines. Accordingly, the infra-red absorption bands of gaseous methane were chosen for the subject of the present investigation.

APPARATUS

For the earlier part of the work a spectrometer designed by W. W. Sleator,³ and used by him in the study of the bands of water-vapor, was available. In this instrument the radiation first passes

¹ "Investigations of Infra-Red Spectra," *Publications of the Carnegie Institution of Washington, D.C.*, p. 39, 1905.

² *Verh. d. D. Phys. Gesell.*, **13**, 796, 1911.

³ *Astrophysical Journal*, **48**, 125, 1918.

through a large rock-salt prism in such a way that only a selected range of wave-lengths is allowed to enter the slit of the grating spectrometer. Thus, overlapping of the spectral orders can be entirely avoided. The source of light was a Nernst glower supplied with power from the university mains. Since the lamp was used during hours when the load on these lines is very small, the voltage fluctuated but little.

The thermopile, constructed by Coblenz, is the one used in previous work with this spectrometer, but the Paschen astatic needle galvanometer, built by Sleator and formerly employed to measure the feeble currents from the thermopile, has been replaced by another of the same type constructed in this laboratory. With the illuminated scale at a distance of 2 m the figure of merit is $84.7 \times 10^{-10} T^{-1.88}$ amperes per millimeter, where T is the time required for the instrument to deflect and return to its original position. For the undamped motion of the suspension, the figure of merit depends upon the inverse square of the period, but with light systems in air the sensitivity varies less rapidly with period. The instrument was always overdamped. Generally, the galvanometer was adjusted to a period of six or seven seconds, corresponding to a figure of merit of 2.5×10^{-10} amperes per millimeter. The resistance, about 2.2 ohms, nearly equals that of the thermopile. Unfortunately, this instrument was not protected from vibrations of the building nor was it shielded magnetically, consequently all readings were taken during the quiet hours between one and five o'clock in the morning.

The grating is an admirable echelette ruled in this laboratory by Dr. Barker. The form of the grooves is such that a large proportion of the energy of the spectral region between 6μ and 8μ is thrown into the first diffracted image. The spacing, 2800 lines per inch, gives good dispersion in this region but, of course, is not so satisfactory for shorter wave-lengths. The ruled area measures 10×16 cm, and covers all but a narrow margin of the polished surface.

Another spectrometer designed by E. F. Barker¹ served for work at shorter wave-lengths. Except for a slight change in the use of the prism, the arrangement is similar to the one just described. The thermopile, however, has a considerably higher resistance (14.5

¹ *Astrophysical Journal*, 55, 391, 1922.

ohms), and is connected to a Leeds and Northrup high-sensitivity galvanometer of the D'Arsonval type. This detecting system proved to be very satisfactory. Although not so sensitive as the apparatus previously used, it is much more stable. When the scale is at a distance of 1 m from the mirror, the galvanometer has a figure of merit of 2.4×10^{-9} amperes per millimeter, but was considerably overdamped, twenty seconds being required for a single deflection. When the size of the deflections permitted, a critical damping resistance of 19 ohms was added to the 26.5 ohms already in the circuit. The advantage of a quick and definite throw more than offset the decrease in deflection.

Again, one of Dr. Barker's echelettes ruled with 7200 lines to the inch proved most valuable, particularly in the region from 2μ to 4μ . The effective surface is 13 cm long by 8 cm high. The glower, supplied from the Detroit Edison Company's 220-volt mains and ballasted with a large resistance, was fairly steady even during hours when other loads were on the line.

Not fewer than twelve cells ranging in length from $\frac{1}{2}$ mm to 30 cm were used as containers for the absorbing gas at various times in the progress of the investigations. Nearly all of the cells were hollow brass cylinders with thin sheets of mica for ends. Soft wax cements the mica to the brass and prevents the leakage of gas. These mica windows had a thickness of about 0.04 mm and were sufficiently transparent, except between 8μ and 9μ . For this region polished plates of rock salt replaced the mica.

METHODS AND RESULTS

Methane was generated by heating together in an iron crucible a mixture of two parts by weight of soda lime (CaO , 67 per cent, and Na_2O , 33 per cent) and one part of fused anhydrous sodium acetate. Since the chemicals contained only very small traces of impurities (about 0.01 per cent), no further attempt was made to purify them. The gas generated in this way bubbled through two washing towers of sodium hydroxide solution and five towers of concentrated sulphuric acid. Thus the methane was freed from impurities, principally water-vapor and ethylene, which may be present. The cells were filled by downward displacement of air and, after a volume of gas several

times as large as the capacity of the absorption chamber had passed through, the openings were tightly closed. The cells containing methane generally occupied a position just in front of the first slit of the prism spectrometer. Since the mica windows of the cell absorb some of the radiation, it is necessary to introduce compensating windows into the beam when the cell is removed. The most satisfactory results were obtained when the compensating windows and the windows of the cell were cut from the same sheet of mica.

In the actual measurements the grating and prism were turned to positions appropriate to the wave-length under investigation, and the galvanometer deflections produced by opening the shutter were read both when the cell was in the beam and when it was replaced by the compensating windows. For each position of the grating, from eight to sixteen such readings were taken. These data properly reduced give the fraction of the incident energy absorbed by the gas. The same procedure repeated at intervals approximating 0.001μ furnished curves such as those shown in Figures 1, 2, and 3.

Thus, the single maximum of absorption observed by Coblentz at 7.7μ resolves into thirty or more lines with a very intense region of absorption at the center. Figure 2 presents, in part, the analysis of the band near 3.31μ . Here about sixty lines have been measured. Figure 3 indicates that the region of 2.35μ is more complicated than the other bands and that evidently the resolving-power is insufficient to reveal the fine structure.

With the 2800-line grating visual methods of calibration fail and the mercury line at 1.0140μ does not possess measurable intensity. Several calibrations were made, however, by means of the lines $+6$ to -6 in the band of hydrogen chloride at 3.46μ , for which accurate wave-lengths have been published by W. F. Colby and C. F. Meyer.¹ Thus in the equation

$$n\lambda = K \sin (\theta - \theta_0)$$

$\log K$ is $1.24516 + 0.000011 (t - 20)$ where t is the temperature of the grating. The position of the central image was determined at the beginning and again at the end of each day's work. The 7200-line grating gave sufficient energy so that even with the D'Arsonval

¹ *Astrophysical Journal*, 53, 300, 1921.

galvanometer measurements were possible on the first-, second-, and third-order spectra of the mercury line mentioned above. Sixteen calibrations yielded a mean value of $0.847208 + 0.0000074 (t-20)$

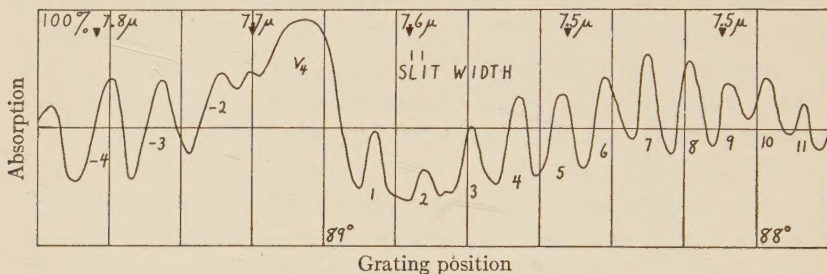


FIG. 1.—A portion of the band at 7.7μ

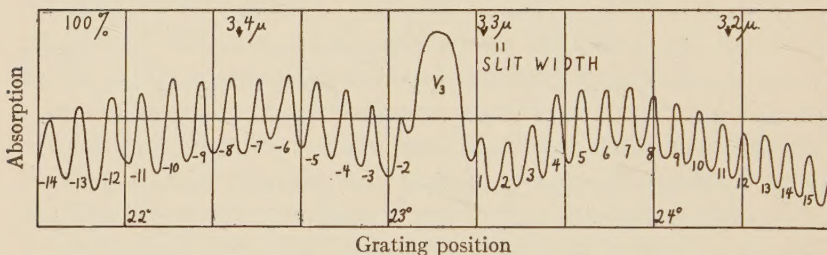


FIG. 2.—Portion of the band at 3.31μ

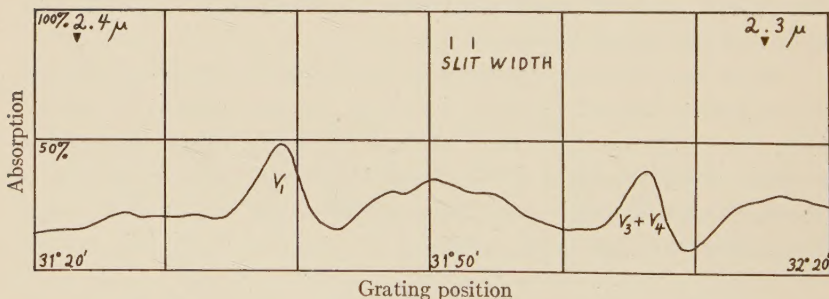


FIG. 3.—Band at 2.35μ

for $\log K$, in good agreement with 0.847207 arrived at several months before by Dr. Barker from measurements on the bands of hydrogen chloride. The temperature corrections were computed from coefficients of expansion for the material on which the gratings were ruled.

The slits of the spectrometers were usually adjusted to a width

of $\frac{1}{2}$ mm. A short calculation shows that with the 2800-line grating the slit of the thermopile includes ranges of 86, 84, and 70 Å, respectively, in the first-order spectra at 2.35 μ , 3.31 μ , and 7.7 μ . With the 7200-line grating the thermopile slit includes 27 Å at 3.31 μ and 31 Å at 2.35 μ .

TABLE I
REGION OF 7.7 μ MEASURED WITH 2800-LINE GRATING

<i>m</i>	Intensity (5.0-cm Cell)	Wave-Length	Frequency
— 12.....	5	8.0802 μ	1237.6 cm ⁻¹
11.....	5	8.0469	1242.7
10.....	6	8.0111	1248.3
9.....	5	7.9708	1254.6
8.....	6	7.9296	1261.1
7.....	5	7.8974	1266.2
6.....	5	7.8677	1271.0
5.....	6	7.8287	1277.4
4.....	7	7.7913	1283.5
3.....	7	7.7569	1289.2
— 2.....	7	7.7140	1296.3
(App. V ₄).....	10	7.6672	1304.3
1.....	5	7.6203	1312.3
2.....	3	7.5929	1317.0
3.....	5	7.5583	1323.0
4.....	6	7.5283	1328.3
5.....	6	7.5000	1333.3
6.....	7	7.4722	1338.3
7.....	8	7.4463	1342.9
8.....	8	7.4193	1347.8
9.....	7	7.3936	1352.5
10.....	7	7.3708	1356.7
11.....	6	7.3463	1361.2
12.....	5	7.3234	1365.5
13.....	5	7.3017	1369.5
14.....	4	7.2761	1374.4
15.....	3	7.2557	1378.2
16.....	2	7.2289	1383.3
17.....	2	7.2071	1387.5
18.....	2	7.1806	1392.6
19.....	2	7.1615	1396.4
20.....	2	7.1381	1400.9
21.....	1	7.1151	1405.5

Table I gives the wave-lengths, frequencies, and intensities for the lines in the band at 7.7 μ as measured with the 2800-line grating. By careful work on the quietest nights observations were made on the spectrum as far as 8.5 μ . When the ordinal numbers of the lines are chosen as shown in the table the frequencies may be represented by

$$\nu = 1320.4 + 5.409 m - 0.0377 m^2.$$

TABLE II
REGION OF $3.31\ \mu$ MEASURED WITH 7200-LINE GRATING

Designation	Intensity (6.6-cm Cell)	Wave-Length	Frequency
(App. 2 V_4).....	2	$3.8466\ \mu$	$2599.7\ \text{cm}^{-1}$
-XI.....	1	3.7636	2657.0
X.....	1	3.7450	2670.2
IX.....	1	3.7269	2683.2
VIII.....	1	3.7075	2697.2
VII.....	2	3.6873	2712.0
VI.....	2	3.6667	2727.2
V.....	3	3.6462	2742.6
-26.....	1	3.6358	2750.4
IV.....	2	3.6257	2758.1
III.....	2	3.6063	2772.9
II.....	3?	3.5847	2789.6
-22?.....	3?	3.5807	2792.7
.....	2	3.5710	2800.3
-I.....	3?	3.5643	2805.6
(App. V_2+V_4).....	3	3.5409	2824.1
I?.....	2?	3.5254	2836.6
-17?.....	1?	3.5168	2843.5
16.....	3	3.5027	2854.9
15.....	4	3.4896	2865.7
14.....	5	3.4771	2876.0
13.....	6	3.4648	2886.2
12.....	6	3.4520	2896.9
11.....	6	3.4397	2907.2
10.....	7	3.4271	2917.9
9.....	7	3.4153	2928.0
8.....	7	3.4035	2938.2
7.....	7	3.3915	2948.5
6.....	7	3.3799	2958.7
5.....	7	3.3682	2968.9
4.....	6	3.3566	2979.2
3.....	6	3.3453	2989.3
-2.....	5	3.3336	2999.8
(App. V_3).....	9	3.3185	3013.4
1.....	4	3.3012	3029.2
2.....	4	3.2905	3039.1
3.....	5	3.2800	3048.8
4.....	6	3.2700	3058.1
5.....	6	3.2598	3067.7
6.....	6	3.2499	3077.0
7.....	7	3.2400	3086.4
8.....	6	3.2306	3095.4
9.....	6	3.2208	3104.8
10.....	6	3.2115	3113.8
11.....	5	3.2023	3122.8
12.....	5	3.1932	3131.7
13.....	4	3.1843	3140.4
14.....	4	3.1755	3149.1
15.....	3	3.1667	3157.9
16.....	3	3.1580	3166.6
17.....	2	3.1493	3175.3
18.....	2	3.1416	3183.1
19.....	1	3.1328	3192.0
20.....	1	3.1257	3199.3
21.....	0	3.1168	3208.4
22.....	0	3.1096	3215.8
23.....	0	3.0991	3226.7
24.....	0	3.0909	3235.3

Three complete sets of readings were made with the 2800-line grating on the band at 3.31μ and three more with the 7200-line grating. Table II summarizes the results. Again the method of least squares was employed to fit the data to the parabolic formula

$$\nu = 3019.3 + 9.771 m - 0.0351 m^2.$$

Neither the 2800- nor the 7200-line grating revealed any definite fine structure in the region of 2.35μ , but Table III contains the wave-lengths of the few measurable absorption maxima.

TABLE III
REGION OF 2.35μ MEASURED WITH 7200-LINE GRATING

Designation	Intensity (6.6-cm Cell)	Wave-Length	Frequency
(App. $V_3 + 2V_4$)	1	2.4262 μ	4121.7 cm^{-1}
(App. V_1)	5	2.3714	4216.9
(App. $V_3 + V_4$)	4	2.3178	4314.4
(App. $V_2 + V_3$)	1	2.2008	4543.8

CONCLUSIONS

While the general question of interpretation is left to Dr. Denison, whose paper follows, it will not be amiss to point out certain peculiarities of structure which distinguish this band system from those previously observed. The regions of intense absorption near the centers of the bands mapped in Figures 1 and 2 are evidently unresolved zero branches, similar to those observed in the photographic regions of the spectrum; while the positive and negative branches are seen on either side of the center. Other experimenters, notably Burmeister,¹ have found bands of this general description, but under the lower resolving-powers used by them the true character of the absorption was not so apparent. Computation indicates that the spacing between the lines of the zero branch is far too small to be detected by the apparatus. It was shown in another way, however, that this maximum is not a simple line but a band. If a series of lines such as the positive branch in Figure 2 is mapped for various increasing thicknesses of absorbing gas it is found that the center of gravity of the system as a whole shifts toward higher values of $|m|$. This is the effect observed by Angstrom in unresolved bands. The explanation is simple. For a moderate length of absorbing gas the most intense

¹ *Verh. d. D. Phys. Gesell.*, **15**, 589, 1913.

lines for methane at room temperature are near $|m|=6$. If the absorption cell is exchanged for a much longer one, the percentage of absorption at the strongest lines, being already so great, cannot increase much; whereas the lines of higher number become many times more intense. Hence the center of gravity of the band shifts toward

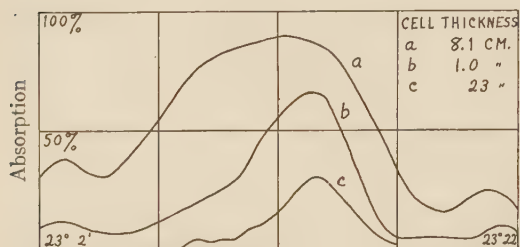


FIG. 4.—Showing shift of the zero branch at 3.31μ

lines of higher ordinal number. This effect for the zero branch at 3.31μ is shown in Figure 4. It appears, also, that the zero line of this series falls on the zero line of the positive and negative branches.

The frequency difference between adjacent lines near 3.31μ is 9.77 cm^{-1} and near 7.7μ it is 5.41 cm^{-1} . Furthermore a rather faint series, designated in Table II by Roman numerals, has been found near 3.5μ . This band has the peculiarity, here observed for the first time in the infra-red region, of converging to a head on the side of the band toward longer wave-lengths. The frequency differences for these lines are about 15.3 cm^{-1} , which is nearly the sum of the frequency differences mentioned above. On the basis of the quantum theory the moment of inertia of the molecule is given approximately¹ by

$$I = \frac{h}{4\pi^2(\Delta\nu)}$$

where h is Planck's constant and $\Delta\nu$ the frequency difference between adjacent lines in the band spectrum. The foregoing frequency differences for the three sets of bands give for the moments of inertia of the molecule of methane 5.66×10^{-40} , 10.2×10^{-40} , and 3.61×10^{-40} gm cm², respectively. Furthermore, the formula

$$I = \frac{\frac{3}{2}RT}{4\pi^2 N \bar{\nu}_r^2}$$

given by Eucken,² in which $R/N = 1.372 \times 10^{-16}$ ergs per degree, T the absolute temperature, and $\bar{\nu}_r$ the most probable rotational frequency

¹ A. Kratzer, *Annalen der Physik*, **67**, 127, 1922.

² *Zeits. Elektrochem.*, **26**, 377, 1920

of the methane molecule, affords a rough check on these numbers. $\bar{\nu}_r$ is here interpreted as one-half of the frequency difference between the most intense line of the positive branch and the corresponding line of the negative branch. This quantity cannot easily be determined from grating spectra, but the best values available yield 4.3×10^{-40} and 11×10^{-40} gm cm², corresponding to the first two values above.

Guye and Rüdý¹ recently calculated the diameter of the molecule of methane from electrical measurements. Their result is somewhat larger than those deduced from the foregoing moments of inertia, but due to the uncertainty in the meaning of the term "diameter" no exact check is to be expected. Measurements of viscosity furnish a molecular diameter slightly less than that given by Guye and Rüdý.

Much remains to be done in mapping the absorption spectrum of methane, and with the help of more efficient apparatus now in process of construction the author hopes soon to carry the task more nearly to completion.

Methane was not the only substance investigated. Diligent search for the "first harmonic" of hydrogen fluoride revealed no measurable absorption even with cells 1 m in length. Next, the spectrum of hydrogen iodide was explored in the region between 2 μ and 6 μ with no better success. Since then, Schäfer and Thomas² announced the discovery of a rather faint unresolved band for hydrogen fluoride near 1.25 μ , the position predicted by Imes. The same investigators were unable to find any trace of infra-red absorption for hydrogen iodide.

In conclusion, the writer wishes to express his indebtedness to Professor Randall, under whose direction the work here presented was done. Dr. Sleator and Dr. Barker gave valuable suggestions on experimental technique and also on the interpretation of the results. During his visit to the university in 1922 Professor Arnold Sommerfeld examined the data then available and discussed the meaning of the bands from the standpoint of quantum mechanics.

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UNIVERSITY OF MICHIGAN
December 22, 1924

¹ *Comptes Rendus*, **174**, 382, 1922.

² *Zeitschrift für Physik*, **12**, 330, 1923.

